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2006 Chinese Phys. Lett. 23 3029

(http://iopscience.iop.org/0256-307X/23/11/040)

Effect of Molecular Weight on Liquid Crystal Photoalignment by Photosensitive Polyester Containing Thrifluoromethyl Moieties *

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(Received 26 July 2006)

We investigate the liquid-crystal (LC) alignment direction on photoalignment films formed from photosensitive polyester containing thrifluoromethyl moieties (PPDA) with various molecular weights by crossed polarized optical microscopy. It is found that LC alignment behaviour changes with molecular weight of PPDA. The LC alignment on PPDA irradiated films with the highest molecular weight is homogeneous, while those with low and intermediate molecular weights are homeotropic. However, surface morphologies show weak dependence on molecular weight. The surfaces are smooth and there is no clear morphological anisotropy on these aligned films observed by an atomic force microscope. The surface energies of the irradiated films are also measured by using an indirect contact-angle method where both surface energy and its polar component increase with increasing molecular weight. Different polar surface energies can be considered as a main reason for different alignment characteristics.

PACS: 61. 30. Hn, 68. 55. Jk, 82. 35. Gh

In the liquid crystal (LC) display industry, the unidirectional mechanical rubbing technique is almost exclusively applied to align LCs. However, this traditional rubbing technique has many drawbacks, such as sample contamination, static charge generation, and scratches. The photoalignment technique can be used not only to avoid these problems, but also to fabricate multi-domains to overcome the intrinsic viewing angle problem of LC display devices.[1−4] Thus, the photoalignment technique has received much attention in viewpoints of both scientific and practical interest.

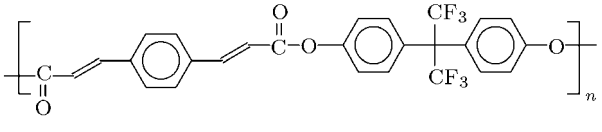

Fig. 1. Chemical structure of PPDA.

Many natures of the photoalignment technique have been studied in detail, such as photochemistry, stability, and electro-optical characteristics.[5,6] However, the effect of molecular weight on photoalignment has not been independently studied, although molecular weight can affect many characters of polymer, e.g. transition temperature, viscosity and equilibrium morphology of the LC alignment film.[7] In this Letter, the effect of molecular weight on LC photoalignment by photosensitive polyester containing trifluoromethyl moieties (PPDA) is investigated and the chemical structure of PPDA is depicted in Fig. 1. It is found that the photoalignment films of PPDA with lower or higher molecular weight would induce homeotropic or homogeneous alignment of LCs, respectively. Here, how the molecular weight of PPDA affects the mechanism of LC alignment on a thin film formed from PPDA would be examined.

PPDA was synthesized similarly to our previous study,[8] which could be divided by tetrahydrofuran (THF) and N,N-Dimethylformamide (DMF): the component (PPDA-1), which can be dissolved in THF, has the lowest molecular weight; the component (PPDA-2), which cannot be dissolved in THF while can be dissolved in DMF, has immediate molecular weight; the rest (PPDA-3), which cannot be dissolved in both solvents, has the highest molecular weight. The molecular weight was measured by gel permeation chromatography experiment, as shown in Table 1. PPDA-n ($n = 1, 2, 3$) with 1 wt.% were dissolved with THF, DMF and N-methyl-2-pyrrolidone (NMP), respectively. Each solution was spin-coated onto indium tin oxide (ITO) glass substrates and immediately irradiated by linearly polarized ultraviolet light (LPUVL) from 300 W Hg–Xe lamp with a Glan-Thomson prism at room temperature. A 280-nm filter (Model 58600 ORIEL) was used to obtain the desired ultraviolet wavelength. The incident light was perpendicular to the film surface and the intensity was 1.0 mWcm^{-2}. All the PPDA films were irradiated under the LPUVL with 0.9 Jcm^{-2}, because the align-

* Supported by the National Natural Science Foundation of China under Grant Nos 60277033 and 50473040, and the Science Foundation of Jilin Province under Grant Nos 20020603 and 20050520.

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ment of LCs is uniform and stable at this case. The LC cells (cell gap=40 μm) were fabricated with two irradiated PPDA-coated substrates. The commercial LC material 4-cyano-4-n-pentylbiphenyl (5 CB) ($T_{NI} = 35.4°C$, Aldrich) was injected into the cells at 36° C. The cells were then cooled to room temperature where 5 CB exhibited nematic phase.

Table 1. Equivalent molecular weights of PPDA-n. PD: polydispersity index; M_w: weight-average molecular weight, M_n: Number-average molecular weight.

Materials	M_n	M_w	PD
PPDA-1	2019	2263	1.121
PPDA-2	10586	13645	1.289
PPDA -3	> 10586		

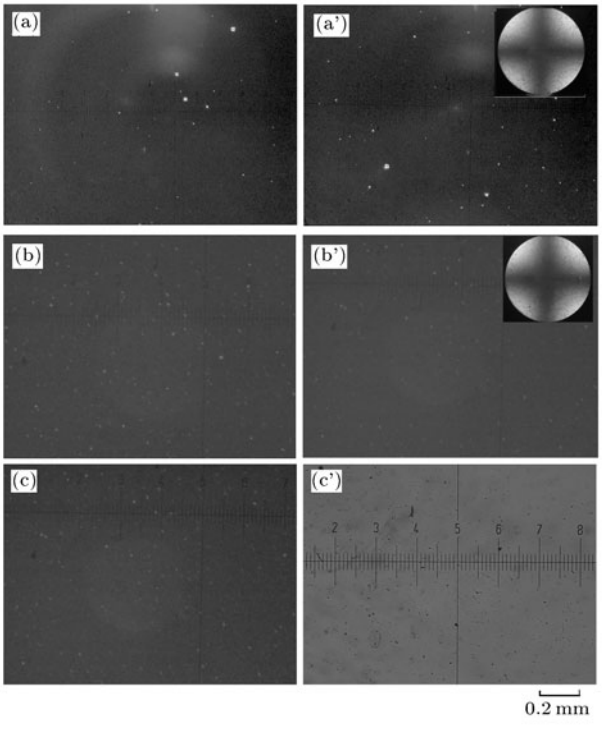

Fig. 2. Polarized optical micrographs of LC cells: (a) and (a′) PPDA-1; (b) and (b′) PPDA-2; (c) and (c′) PPDA-3. Here (a)–(c) are obtained with the electric field vector E of the incident LPUVL parallel to one of the polarizer axes; and (a′)–(c′) are taken with the vector E at 45° to each polarizer axis. The inset shows the dark cross brush observed by a conoscope microscope.

The photoalignment of 5 CB on these irradiated films was studied using the crossed polarized optical microscopy. Figure 2 shows the polarized microphotographs of the LC cells. The LC alignment on the films with PPDA-1 was uniform, and the dark state of the light did not change upon rotation of the sample, as shown in Figs. 2(a) and 2(a′). This is because the axis of the homeotropically aligned LC molecules is perpendicular to the irradiated films. Apart from that, the dark crossed brush appeared through conoscope observation, which is a significant character for homeotropic alignment, as shown in the inset of Fig. 2(a′). Obviously, the irradiated films of PPDA-1 induced LC homeotropic alignment. It is the same case for PPDA-2, seeing Figs. 2(b) and 2(b′). In the case of the PPDA-3 film, there was a different phenomenon. The light state changed upon rotation of the cell, as shown in Figs. 2(c) and 2(c′). The dark state of the light through the cell appears with the electric field vector E of the incident LPUVL parallel to one of the polarizer axes and the bright state appears with the vector E at 45° to each polarized axis. Therefore, we can validate the irradiated films of PPDA-3 induce homogeneous alignment of LCs.

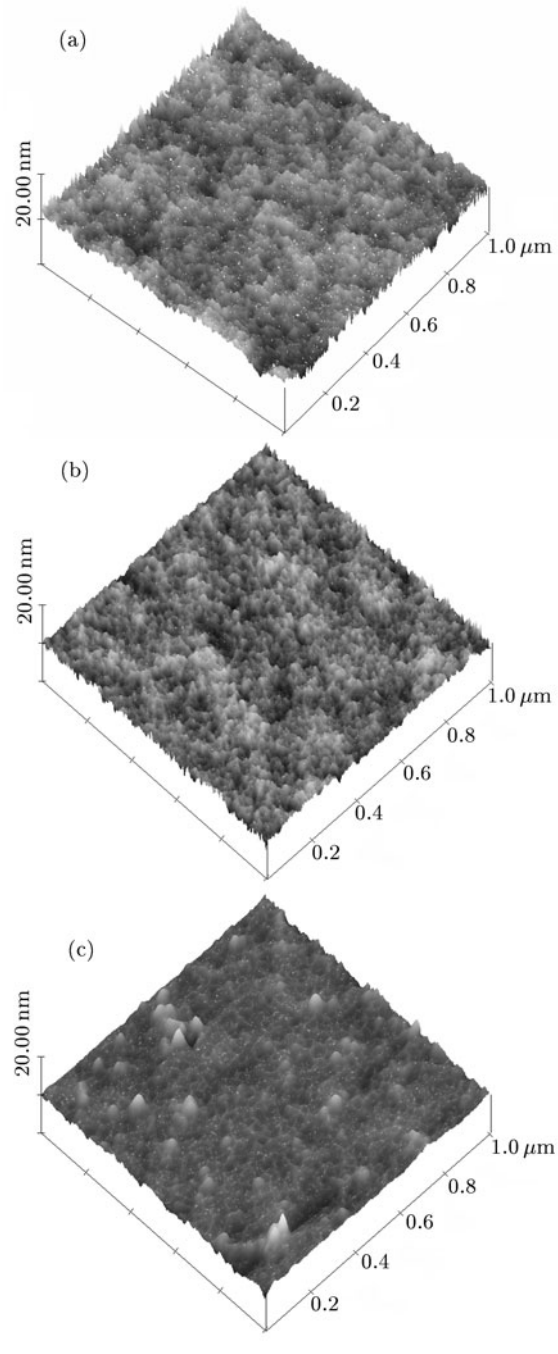

Fig. 3. AFM images of PPDA films with various molecular weights irradiated with 0.9 Jcm^{-2}: (a) PPDA-1; (b) PPDA-2; (c) PPDA-3.

The surface morphology was determined by an atomic force microscope (AFM) (Nanoscope 3, Digital Instrument). Some representative AFM images of irradiated PPDA films were shown in Fig. 3. It can be found that the surface images do not vary significantly with the molecular weight of the PPDA samples, and their root-mean-square (rms) surface roughnesses are in the range 0.22–0.30 nm. These surface roughnesses are relatively much smaller than those previously reported for PI films,[9,10] which indicate that the surfaces of irradiated PPDA films are smooth. However, there was no significant topography on the surface images, which was often observed on rubbed PI films. Moreover, we could not judge the LC alignment direction from surface images. Therefore, the roughness of the aligned films was so small that it should have little effect on the photoalignment behaviour of the films.

To clarify the reason for different LC alignments on irradiated PPDA films, surface energies were measured using the indirect contact-angle method and calculated according to the Owens–Wendt–Kaelble–Young equation:

$$\gamma_L^t(1+\cos\theta) = 2(\gamma_L^d\gamma_S^d)^{1/2} + 2(\gamma_L^p\gamma_S^p)^{1/2},$$

where θ is Young's contact angle; γ^d and γ^p are respectively the dispersion and polar components of surface energy, $\gamma^t = \gamma^d + \gamma^p$. Two liquids used for contact angles were water and glycerol: $\gamma^d_{\text{water}} = 21.8\,\text{mJm}^{-2}$, $\gamma^p_{\text{water}} = 51.0\,\text{mJm}^{-2}$, $\gamma^d_{\text{gloycerol}} = 37.0\,\text{mJm}^{-2}$, $\gamma^p_{\text{glycerol}} = 26.4\,\text{mJm}^{-2}$.[11] Hence, total surface energy γ_S^t and polar surface energy γ_S^p of the irradiated films can be calculated.

The contact angle experiments of water and glycerol were performed using an environmental chamber at 20°C. To obtain reliable contact angle data, at least three droplets in different regions of the same film piece were dispensed for contact angle measurement, and at least two film pieces were used. Thus, at least six contact angles were averaged for each kind of films as well as each kind of liquids. The contact angle and surface energy data of the three films with different testing liquids are listed on Table 2.

Table 2. Surface energies of PPDA irradiated films with various molecular weights.

Materials	Irradiation energy (Jcm^{-2})	θ_{water} (deg)	θ_{glycerol} (deg)	γ_S^t (mJm^{-2})	γ_S^p (mJm^{-2})	γ_S^p/γ_S^t
PPDA-1	0.9	84 ± 1	63 ± 1	40.93	2.34	5.7%
PPDA-2	0.9	77 ± 1	66 ± 1	41.54	20.12	48.4%
PPDA-3	0.9	32 ± 1	38 ± 1	64.34	55.17	85.7%

As shown in Table 2, it is clear that surface energy of the irradiated film increases with increasing molecular weight, which is consistent with the former results.[12] PPDA-1 and PPDA-2 with lower molecular weights have larger contact angles and smaller total surface energies ($40.93\,\text{mJm}^{-2}$, $41.54\,\text{mJm}^{-2}$). Moreover, we found that their polar surface energies ($2.34\,\text{mJm}^{-2}$, $20.12\,\text{mJm}^{-2}$) are small. Polar surface energy of the alignment layer is very important for LC alignment and can affect the pretilt angle dramatically.[13] As polar surface energy of the alignment layer decreases, the interaction between LC and the alignment film becomes weaker and then the pretilt angle increases, which is similar to the results of Sung *et al.*[14] and Yu *et al.*[15] Akiyama reported that homeotropic alignment of LC is caused by the weak polar anchoring nature.[16] Therefore, in the case of PPDA-1 and PPDA-2 irradiated films, weak polar surface energy should play an important role in homeotropic alignment of LCs.

PPDA-3 has the highest surface energy of $63.34\,\text{mJm}^{-2}$ and γ_S^p/γ_S^t is 85.7%. The higher polar surface energy increases the interaction between LC and the alignment film, which may draw back the LCs onto the plane of the film. Thus, LC molecules are aligned homogeneously on the irradiated PPDA-3 coated substrate.

The thermal stability of the photoalignment generated by irradiated films of PPDA-n is also influenced by the molecular weights. The alignment induced by LPUVL of an exposure energy of $0.9\,\text{J/cm}^2$ is maintained even after heating at 110°C for 10 min when substrate surfaces are coated with PPDA-1. Under the same exposure conditions, the LC cells coated with PPDA-2 and PPDA-3 have higher aligning stability and held their contrast ratio up to 120°C and 135°C, respectively. The films with greater molecular weights have a greater T_g, which is in agreement with the previous publications.[7]

In conclusion, PPDA-n photoalignment films can exhibit LC alignment directions that are significantly dependent on molecular weight. The irradiated films of PPDA-3 with the highest molecular weight induced homogeneous alignment, while those of PPDA-1 and PPDA-2 with lower molecular weight induced homeotropic alignment. The surface morphologies of PPDA-n irradiated films are independent of the molecular weight. All the surfaces are smooth and there is no clear morphological anisotropy on these aligned films observed by an AFM. However, the surface energies show dependences on the molecular weight: PPDA-1 and PPDA-2 with lower molecular weight have lower surface energy and polar energy, which result in homeotropic alignment of LCs; while

for PPDA-3, its surface energy and polar surface energy are larger than those of PPDA-1 and PPDA-2, and the large polar surface energy results in the homogeneous alignment. At the same time, it is found that the thermal stability of PPDA-n films increases with increasing molecular weight.

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